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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| (51) International Patent Classification ⁵ : H01B 1/22 | A1 | (11) International Publication Number: WO 93/24934 (43) International Publication Date: 9 December 1993 (09.12.93) |
| (21) International Application Number: PCT/GB93/01161 (22) International Filing Date: 1 June 1993 (01.06.93) (30) Priority data: 9211500.5 30 May 1992 (30.05.92) GB (71) Applicant (for all designated States except US): FIRST CLASS SECURITIES LIMITED [-/-]; Craigmur Chambers, Road Town, Tortocla (VG). (72) Inventors; and (75) Inventors/Applicants (for US only): SLIFKIN, Michael, Arthur [GB/GB]; 25 Moorside Road, Salford M7 0PJ (GB). HAMPSHIRE, Michael, John [GB/GB]; 3 Brookfield, Upper Hopton, Mirfield WF14 8HL (GB). | (74) Agents: DOWNEY, William, Gerrard et al.; Wilson, Gunn & Ellis, 41-51 Royal Exchange, Cross Street, Manchester M2 7BD (GB). (81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> | |
| (54) Title: ELECTRICALLY CONDUCTIVE PASTES (57) Abstract Pastes for use in the production of a highly electrically conductive thick film cured by ultraviolet radiation with the primary application of screen printing interconnective patterns suitable for electronic circuits comprise a chemical which contracts on polymerisation and a metal powder pigment in the form of spherical particles. The particles advantageously comprise nickel coated with gold or silver. Metal spheres enable radiation reflected from their surfaces to penetrate the matrix to promote efficient polymerisation. The sphere size is advantageously linked to the thickness of the screen. For example, the sphere size is 4 to 15 µm for a screen thickness of 25 µm. | | |

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ELECTRICALLY CONDUCTIVE PASTES

The present invention relates to pastes for use in the production of a highly electrically conductive thick film cured by uv radiation with the primary application of screen printing interconnective patterns suitable for electronic circuits. The field is currently served by thermally cured pastes or inks which have a high content of silver flake. Whilst the conductivity is good being as low as 0.05m cm, the films suffer from two disadvantages. Firstly, containing such a high level of silver flake they are expensive and secondly, being thermally cured, the process is long, typically 6 to 10 minutes. This curing time makes for slow processing with the associated costs and the energy costs are also high. The current invention sets out to reduce the costs of the metal pigment or filler and to produce a uv - cured matrix which has a curing time typically of seconds rather than minutes.

Attempts to produce a uv-cured ink with flake shaped pigments have not met with success. It is believed that the geometrical stacking of plates prevents the penetration of uv radiation between the flakes and hence satisfactory polymerisation is not achieved.

According to the present invention there is provided

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a paste comprising at least one chemical which contracts on polymerisation together with metal powder pigment substantially of a spherical geometry with an outer surface of a metal which either does not oxidise or produces a very thin stable oxide.

Advantageously, the metal of the pigment is ferromagnetic, preferably nickel powder.

The size of the spheres advantageously matches the thickness and definition requirements of the screen printing process. For 25 μ m thick films a particle size distribution from 4 μ m to 15 μ m has been found to be successful.

The provision of a metal surface which, when oxidised, produces a very thin stable oxide enables electrons to tunnel through the dielectric layer between the metal spheres. Coatings which do not oxidise, the noble metals such as gold (Au) for example, are, of course, very suitable. Silver (Ag) produces a thin stable oxide and is most suitable. Copper (Cu) on the other hand does not have a suitable oxide.

Copper spheres are attractive on a resistivity and cost basis although adhesion of other metal coatings may in some cases be difficult. On the other hand adhesion

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of silver (Ag) to nickel (Ni) is good and this has been shown to be a successful combination, namely that of silver (Ag) coated nickel (Ni) spheres.

The use of nickel (Ni) spheres in conductive thick film sheets has a further major advantage, in that the ferromagnetic nature of Ni reduces the wavelength of any electromagnetic waves propagating through the film. The film, therefore, has a smaller skin depth and hence attenuates an electromagnetic wave more effectively. The attenuation coefficient, a , of an electromagnetic wave of angular frequency, w , through a film of resistivity, p , and permeability, μ , is given by

$$a = \sqrt{(w\mu/p)}$$

As the relative permeability of pure Ni is about 250, then a film largely composed of Ni spheres will be expected to attenuate up to about 15 times more effectively than a non-ferromagnetic film of the same resistivity.

The pigment spheres are advantageously blended with a binding polymer and a photoinitiator to promote the uv curing of the polymer. Further, a diluent is preferably added to generate the appropriate rheology suitable to screen printing. A viscosity in the range of 5 to 150 poise is appropriate. Finally, the formulation benefits from the addition of small amounts of three further

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chemicals to improve adhesion, abrasion resistance and to minimise bubble formation.

The requirements of the basic polymer is important in that for good results the material must contract on curing, such that the pigment sphere are compressed together in the final film so promoting good electrical contact from one sphere to the next. In this respect a satisfactory polymer has been found to be urethane acrylate.

In order that the invention may be more clearly understood, one embodiment will now be described by way of example.

The embodiment comprises the following formulation (as a percentage by weight)

| | |
|--|--------|
| Silver coated nickel spheres 4 to 15 μ m | 44.15g |
| Urethane Acrylate | 1.25g |
| Acrylic monomer viscosity modifier | 3.35g |
| Photoinitiator | 0.8g |
| Additives | 0.5g |

This produces a film with a resistivity of 0.3m Ω cm, after curing for a few seconds in uv radiation from a medium pressure Hg lamp with a power of 125W at a

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distance of about 20cms from the sample. The major uv emission from the medium power lamp is at a wavelength of 365nm.

Typical chemicals in the formulation could be:-

Photomer 6140 - Aliphatic Polyester Urethane
Acrylate dissolved in Tripropylene glycol
diacrylate.

- * Viscosity modifier 4237 - Tripropylene glycol
diacrylate
both from Harcros Chemicals UK Ltd.
- * Photoinitiator 4265 combination of Acrylic Keytone
with Lucirin TPO, available from Ciba Geigy, Basle,
Switzerland.
- * The additives. Antibubble - blend of surface active
agents in solution including Lecithin and polyvinyl
alcohol, Lanco flow - Acrylic copolymer and
Lanco-Wax TS1778 - modified micronised PTFE wax are
available from Capricorn Chemicals Ltd.

These are used respectively to prevent bubble
formation, to increase adhesion and to improve the
abrasion resistance.

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A post cure treatment is found to significantly reduce the resistivity. It is known that uv radiation promotes polymerisation to about 95%. Further polymerisation can be achieved by a number of methods such as:-

- * Heat treatment
- * Infra Red heating
- * RF heating
- * Electron beam irradiation
- * Higher energy uv radiation from a low pressure Hg lamp with a major emission at 254nm.

Baking the films in an oven for 6 hours at 100°C reduces the resistivity from 0.3m Ω cm to 0.05m Ω cm.

The use of metal spheres overcomes the problem of uv radiation penetration experienced with the prior art flakes by enabling the radiation reflected from their surfaces to penetrate the matrix and promote efficient polymerisation.

It will be appreciated that the above embodiment has been described by way of example only and that many variations are possible without departing from the scope of the invention.

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CLAIMS

1. A paste comprising at least one chemical which contracts on polymerisation together with metal powder pigment substantially of a spherical geometry with an outer surface of a metal which either does not oxidise or produces a very thin stable oxide.
2. A paste as claimed in claim 1, in which the metal powder pigment is fluromagnetic.
3. A paste as claimed in claim 1 or 2, in which the metal powder pigment is nickel.
4. A paste as claimed in any of claims 1 to 3, in which the particle size of the metal powder pigment is linked to the thickness of the screen printing process in which the paste is to be used.
5. A paste as claimed in claim 4, in which the particle size lies in the range $4\mu\text{m}$ to $15\mu\text{m}$ for a screen thickness of $25\mu\text{m}$.
6. A paste as claimed in any preceding claim, in which the surface of the metal is a coating of a noble metal.
7. A paste as claimed in claim 6, in which the noble

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metal is gold.

8. A paste as claimed in claim 6, in which the noble metal is silver.

9. A paste as claimed in any preceding claim in which the metal powder pigment is blended with a binding polymer and a photoinitiator to promote the curing of the polymer.

10. A paste as claimed in any preceding claim, in which a diluent is added having a viscosity in the range of 5 to 150 poise.

11. A paste as claimed in any preceding claim including chemicals to improve adhesion, abrasion resistance and to minimise bubble formation.

12. A paste formulated in accordance with the example described in the specification.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 93/01161

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: H01B 1/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| X | EP, A2, 0174776 (MINNESOTA MINING AND MANUFACTURING COMPANY), 19 March 1986 (19.03.86), page 3, line 9 - page 4, line 8; page 6, line 18 - page 7, line 9 | 1,2,3,6,7,8, 9,11 |
| Y | — | 4,5,10,12 |
| X | EP, A1, 0343836 (POTTERS INDUSTRIES, INC.), 29 November 1989 (29.11.89), column 1, line 26 - column 2, line 23; column 2, line 41 - line 52; column 5, line 7 - line 43, column 6, line 10 - line 18; column 6, line 40 - column 7, line 27 | 1,2,3,6,7,8 |
| Y | column 5, line 44 - column 6, line 1; column 6, line 10 - line 33 | 4,5,9-12 |
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☒ Further documents are listed in the continuation of Box C.

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| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|---|---|-----------------------|
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| X | EP, A1, 0234347 (INTERNATIONAL BUSINESS MACHINES CORPORATION), 2 Sept 1987 (02.09.87), page 2, line 17 - page 1, line 26; page 3, line 38 - line 41; page 4, line 4 - line 19, page 5, line 4 - line 24 | 1,6,7,8,9 |
| Y | | 10 |
| A | | 2,3,4,5,11,12 |
| | --- | |
| X | EP, A2, 0291064 (E.I. DU PONT DE NEMOURS AND COMPANY), 17 November 1988 (17.11.88) | 1,6,7,8 |
| A | | 2-5,9-12 |
| | --- | |
| Y | EP, A1, 0081323 (JOHNSON MATTHEY PUBLIC LIMITED COMPANY), 15 June 1983 (15.06.83), page 1, line 1 - page 4, line 12; page 9, line 9 - line 19; page 11, line 2 - line 18 | 9-11 |
| A | | 1-8,12 |
| | --- | |
| X | Derwent's abstract, No 87-275700/39, week 8739, ABSTRACT OF SU, A1, 1098-441 (KHIMCHENKO YU I), 7 March 1987 (07.03.87) | 1,2,3 |
| A | | 4-12 |
| | --- | |
| A | US, A, 4732702 (MITSUO YAMAZAKI ET AL), 22 March 1988 (22.03.88) | 1-12 |
| | --- | |

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INTERNATIONAL SEARCH REPORT
 Information on patent family members

26/08/93

 International application No.
 PCT/GB 93/01161

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|---|--|
| EP-A2- 0174776 | 19/03/86 | AU-A- 4508585 JP-A- 61066309 US-A- 4546037 | 13/03/86 05/04/86 08/10/85 |
| EP-A1- 0343836 | 29/11/89 | AU-B- 614122 AU-A- 3390889 JP-A- 1320704 US-A- 4857233 | 22/08/91 30/11/89 26/12/89 15/08/89 |
| EP-A1- 0234347 | 02/09/87 | JP-A- 62199611 US-A- 4780371 US-A- 4859268 | 03/09/87 25/10/88 22/08/89 |
| EP-A2- 0291064 | 17/11/88 | DE-A- 3880884 JP-A- 63301274 | 17/06/93 08/12/88 |
| EP-A1- 0081323 | 15/06/83 | CA-A- 1181580 GB-A- 2111072 JP-A- 58104971 | 29/01/85 29/06/83 22/06/83 |
| US-A- 4732702 | 22/03/88 | GB-A,B- 2186577 JP-A- 62275180 NL-A- 8700189 | 19/08/87 30/11/87 01/09/87 |